Development of low-pH cementitious materials for HLRW repositories Resistance against ground waters aggression

J.L. García Calvo [a], A. Hidalgo [a], C. Alonso [a], L. Fernández Luco [b]

[a] Instituto de CC. de la Construcción Eduardo Torroja, CSIC, Serrano Galvache 4, 28033 Madrid, Spain
[b] INTECIN-Universidad de Buenos Aires, Av. Paseo Colón, 850. C1063ACV Buenos Aires, Argentina

Keywords:
Low-pH cements
Hydration (A)
Long-term performance (C)
Radioactive waste (E)

A B S T R A C T

One of the most accepted engineering construction concepts of underground repositories for high radioactive waste considers the use of low-pH cementitious materials. This paper deals with the design of those based on Ordinary Portland Cements with high contents of silica fume and/or fly ashes that modify most of the concrete "standard" properties, the pore fluid composition and the microstructure of the hydrated products. Their resistance to long-term groundwater aggression is also evaluated. The results show that the use of OPC cement binders with high silica content produces low-pH pore waters and the microstructure of these cement pastes is different from the conventional OPC ones, generating C–S–H gels with lower CaO/SiO_2 ratios that possibly bind alkali ions. Leaching tests show a good resistance of low-pH concretes against groundwater aggression although an altered front can be observed.

1. Introduction

The most accepted engineering construction concept of underground repositories for high level radioactive waste requires the use of cementitious materials for different purposes. When conventional Ordinary Portland Cements (OPC) are used to produce concretes for these underground repositories, the contact with the ground waters creates a pore water leachate with a pH as high as 13.5. This alkaline plume of leaching waters might perturb one of the engineered barriers of the repositories, that one composed of bentonite. The accepted solution to maintain the bentonite stability, which is a function of the pH, is to develop cementitious materials that generate pore waters with $pH \leq 11$, because the alteration of the clay components (with the subsequent loss of its swelling ability) is significantly reduced below this pH value [1]. The feasibility of designing and utilizing low-pH cementitious materials in underground repositories for preventing these undesired processes are being investigated [2–13].

The research on low-pH cementitious materials was initially developed in Canada and Japan [14,15], and nowadays it is addressed from different approaches depending on the type of cement used: 1) Calcium Silicate Cements (OPC based), 2) Calcium Aluminates Cements (CAC based), 3) Phosphate Cements (PC) and 4) Magnesia Cements (MC) [2–15].

Several authors [1–5,16] have demonstrated that the interaction of OPC with ground waters producing the hyper-alkaline fluids is due to the leaching of sodium and potassium hydroxides. Once these alkali hydroxides are released, the pH of the pore water solution in the concrete is controlled by the dissolution of one of the main phases of the OPC paste, the portlandite ($Ca(OH)_2$), which is responsible for the alkaline plume with a pH of 12.6. Later on, between pH 12.6 and 10, the dissolution of the calcium from the C–S–H gel takes place [17–20]. Therefore, it is evident that the decrease of the pore fluid pH from the initial state in the pore solution down to values close to 11 implies the use of OPC cements with low content in alkalis and the depletion of the portlandite (the main source of OH^-).

A literature review on this topic shows that to reduce the content of portlandite, mineral admixtures with high silica content should be used [3,15,21–23]. The amount of OPC is reduced and substituted by mineral admixtures with high silica content to decrease the calcium hydroxide formation in the binder. The fabricated blends follow the pozzolanic reaction that consumes $Ca(OH)_2$ [21]. In fact, Cau Dit Coumes et al. [24] showed that a linear relationship between the pore solution pH of low-alkalinity binders and their silica content exists.

The high mineral admixtures contents used in the low-pH binders significantly modify the microstructure and the pore fluid of these cementitious materials as well as their standard properties. Therefore, a better understanding of the hydration of low-pH cementitious materials is needed. This paper deals with the design and the evaluation of the microstructure and the pore fluid evolution of low-pH materials using binary blends based on OPC plus silica fume (SF) and ternary blends based on OPC, SF and fly ashes (FA), suitable for being used in underground radioactive waste repositories.

Furthermore, taking into account the long life expected in this type of repositories, parameters related to the durability of the cementitious materials must be analysed. Therefore, this paper also deals with

the evaluation of the resistance of low-pH cementitious materials to long-term ground water aggression. In recent studies, from leaching analyses in low-pH cementitious materials using deionised water, a release of Ca in the leaching solution has been described, as well as a decalcification process governed by diffusion. The Ca flux was not only balanced by the release of OH^- but also by that of sulfate ions [9,13]. However, the decalcification of the low-pH cement pastes is much slower than that of OPC ones. Apart from a very low CaO/SiO_2 ratio (0.3 to 0.4 for all pastes), a disappearance of ettringite and enrichment in a hydrotalcite-like phase have been reported near the leached surfaces of low-pH cement pastes [13]. In leaching tests made using simulated fresh groundwater [9], leaching of Ca is again clearly recognized. In the present paper, leaching tests have been also used for analysing the modifications made in the microstructure of low-pH concretes and in their pore fluid chemical composition due to their exposure to a constant ground water flow. In order to simulate realistic conditions, the stability in ground waters has been assessed using ground water from the real site of Äspö, in Sweden. Several techniques are compared to estimate the degraded thickness in two types of low-pH concretes.

2. Experimental

2.1. Studies in cement pastes

Several cement pastes were fabricated using an Ordinary Portland Cement, OPC, with low alkali and low aluminate content which has been partially substituted by high contents of mineral admixtures. A mix composed only of OPC was used as reference. The chemical composition of OPC, SF and FA is presented in Table 1. It is obvious that the SF has the highest SiO_2 amount and introduces low CaO percentages in the blend, although the alkali content is similar to the OPC one. However, the FA used introduces more alkalis in the composition and has the highest alumina content; indeed, it has also higher silica content than OPC. Deionised water was used for the preparation of the cement pastes, using a water/binder (w/b) = 0.5 in all of them. All the samples were cured in a chamber at 98% RH and 21 ± 2 °C temperature until the moment of testing. Table 2 summarizes the formulation used in the cement pastes evaluated, indicating the silica content of every blend.

The changes in the composition of the pore fluid and the solid phases at different days of hydration (2, 7, 30, 90 days and 2 years) were determined in the cement pastes. The pore fluid was extracted using the Pore Fluid Expression Technique [25,26]. The ionic composition of the pore fluid was determined, including pH, OH^- (by automatic titration with 0.05 N HCl), Ca, Na, K and SO4 by ionic chromatography, and Si^- by photometry. Besides, the evolution of the pore fluid pH was followed using an ex-situ leaching method, where the pH of a suspension with a solid powder paste/deionized water = 1/1 was measured. This method has previously been calibrated with the Pore Fluid Expression Technique [2].

The hydration of the pastes was determined by stopping the curing at different ages (2, 7, 30, 90 days and 2 years), by means of powdering the samples and removing the free water with ethanol and acetone. DTA/TG tests and XRD analyses have been employed to study the evolution of the microstructure composition of the solid phases in the fabricated pastes. Some pastes were also observed employing Backscattered Electron Microscopy and EDX analyses for determining the C/S ratio of C–S–H gels.

Table 1
Chemical composition (wt.%) of OPC, SF and FA.

	LI	IR	SiO_2	Al_2O_3	Fe_2O_3	CaO (total)	MgO	SO_3	Na_2O	K_2O	CaO (free)
OPC	4.34	1.13	18.0	4.85	5.26	62.4	1.84	3.28	0.18	0.35	1.92
SF	0.09	0.06	91.8	0.59	3.74	1.31	0.93	–	0.15	0.37	0.01
FA	2.19	0.52	54.3	26.9	5.38	4.52	2.24	–	0.61	3.17	0.15

LI: loss of ignition; IR: insoluble residue.

Table 2
Cement formulations used in the fabrication of the pastes.

Sample	OPC (%)	SF (%)	FA (%)	SiO_2 (%) total
Ref	100	–	–	18
B-1	60	40	–	47
B-2	50	50	–	55
T-1	80	10	10	29
T-2	35	35	30	51
T-3	20	50	30	65

2.2. Water aggression resistance of low-pH concretes

The resistance against ground water aggression was evaluated in two types of low-pH concretes:

1) Basic concrete (BC): several samples with a $\phi = 5$ cm (test requirement) were fabricated for analysing the ground water aggression resistance of low-pH cements in concretes with a "conventional" mix composition.
2) Cores ($\phi = 5$ cm) extracted from a real shotcreted low-pH concrete plug fabricated in Äspö facilities for evaluating the water aggression resistance of low-pH cements in a real application (called SC in the paper). The fabrication of this shotcreted plug required an additional design [27].

The materials used in the fabrication of the low-pH concretes were:

- A low-pH cement formulation based on OPC: 60%OPC–40%SF (used also in the B-1 cement paste fabricated).
- Aggregates from Äspö facilities. The granulometry of the three fractions was: 0–4 mm (sand), 4–8 mm (medium) and 8–12 mm (coarse). In the case of the basic concrete only the two smaller fractions were used.
- Additives: a Naphthalene Formaldehyde Superplasticizer, a conventional air-entraining admixture (and an alkali free accelerator from Sika for the shotcreted plug).

Table 3 shows the nominal composition of both types of concretes. The material behaviour under the long-term action of water, in representative conditions of the real repository scenario, has been evaluated in both concrete types. The accelerated test helps to reproduce the sequence of degradation processes.

Cylindrical samples ($\phi = 5$ cm; $h = 5$ cm) were placed between two cylinders of methactylate containing holes for water inlet and outlet. The block was sealed with an epoxy-resin in order to assure that water passed only through the sample and measured water fluxes were correct. A water head of 0.5 bars pressure was maintained to pass water from the concrete after which it was collected for analysing. In order to

Table 3
Concretes compositions.

Constituents	Basic concrete (BC)	Shotcreted concrete (SC)
Water (kg/m^3)	160	277.2
Binder (kg/m^3) (60%OPC + 40%SF)	320	307.2
Water/binder	0.5	0.9
Coarse agg. (8–12 cm) (kg/m^3)	–	615.6
Medium agg. (4–8 cm) (kg/m^3)	855	199.7
Sand (0–4 cm) (kg/m^3)	1033	818.1
Superplasticizer (kg/m^3)	3.2	5.5
Accelerator (kg/m^3)	–	18.5
Air-entraining admixture (kg/m^3)	–	0.6

Table 4
Composition of the ground water used in the leaching test.

	Cl	SO_4	NO_2^-/NO_3^-	Na	K	Ca	Mg	Si	pH
[mg/l]	2681	232	–	1129	9.36	356	78.2	7.32	8.20

simulate the real conditions, the leaching tests were carried out using granitic water from Äspö, whose chemical composition is presented in Table 4. Fig. 1 shows a scheme of the device used.

Variables measured continuously in every case were: effluent flux (to determine the hydraulic conductivity of the concretes), chemical composition and pH. At the end of experiments (14 months in basic concrete samples and 2 years in cores extracted from the plug) concrete cylinders were divided in three similar size portions (≈1.5 cm); the upper part was in contact with the penetrating water. Each one of these three parts was characterised by BSEM with EDX analyses and phenolphtaleine test.

3. Results

3.1. Formulation of low-pH cements based on OPC plus mineral admixtures with high silica content

3.1.1. Changes in pore fluid composition

The evolution of the pore fluid pH, measured using the ex-situ leaching test 1/1, is showed in Fig. 2. Table 5 shows the pore fluid composition, from pore fluid expression tests, after 90 days and 2 years of hydration.

The higher the silica content of the binder, the lower the pore fluid pH value of the paste. This effect is more relevant for longer curing times (>90 days) because at short ages the pH can be even higher in the low-pH cement pastes, as it has already been described by Larbi et al. [28]. It is remarkable that from 90 days to 2 years, the pore fluid pH remains stable. These results indicate that the percentage of silica in the cement formulation has to be above 45% to obtain a pH bellow 12.5 at 90 days, indicating that the portlandite has been removed from the cement paste as will be shown in the next section, where the solid phases' evolution is evaluated. In binary blends composed by OPC and

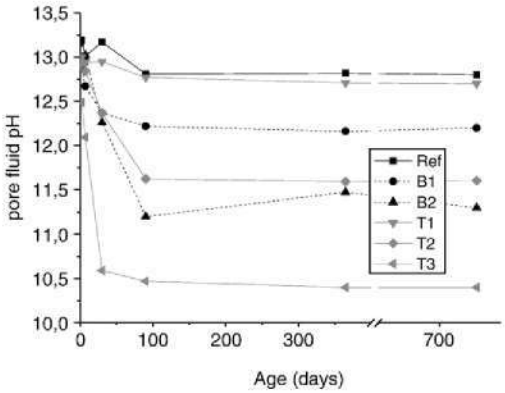

Fig. 2. Evolution of the pore fluid pH of cement pastes (ex-situ leaching method 1/1).

SF, the achievement of this SiO_2 content implies the use of a minimum SF percentage of 40%. These results agree with previous data from literature: Mihara et al. [29] published that large amounts of silica fume (more than 40%) effectively reduces the pH of cement paste leachate but even with incorporation rates above 50% pH remains above 12 due to the presence of residual portlandite [30–32]. Cau Dit Coumes et al. [5] determined that for totally consuming the portlandite content and obtaining pore fluid pH values below 11, total silica contents (including silica from SF, cement and other pozzolanic additions) higher than ≈50% should be used.

In Table 5, a decrease in the alkali concentration in the pore solutions is evident in the binder formulations with high mineral admixtures contents. After 90 days, the Ca concentrations in the pore solutions of the low-pH blends are higher than in the pure OPC. After 2 years the calcium content is lower in the pore solution of low-pH cement pastes. The increase of the sulfate content in the pastes with the lower pore fluid pHs is also very significant as well as the increase in the Si concentrations. Fig. 3 shows the evolution with curing time of the Na, K and Ca contents in the pore solution of the B-1 sample. This figure clearly shows that at short ages in low-pH cements there is a decrease in the alkali content of the pore solution but an increase in the calcium concentrations.

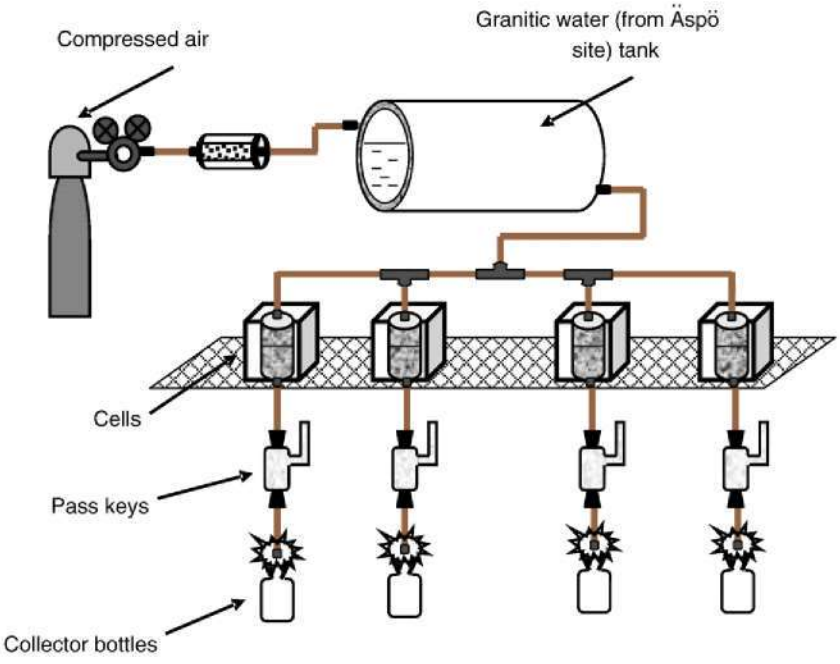

Fig. 1. Experimental set-up for leaching tests.

Table 5
Composition of the pore fluid of low-pH pastes. 90 days and 2 years.

Sample	Age	pH	Chemical composition (mg/l)					
			Na	K	Ca	S	Al	SO_4
Ref	90 days	12.9	603	2130	474	1.23	ND	12.8
	2 years	12.8	200	561	709	ND	0.34	24.5
B-1	90 days	12.2	120	322	612	9.82	ND	84.4
	2 years	12.2	26.2	29.8	329	ND	5.40	67.5
B-2	90 days	11.2	165	369	651	60.3	ND	2180
	2 years	11.3	58.3	51.9	462	1.45	0.89	1080
T-1	90 days	12.6	118	459	690	ND	ND	31.6
	2 years	12.7	84.6	305	684	ND	0.94	32.6
T-2	90 days	11.2	175	388	486	48.0	ND	182
	2 years	11.6	81.0	78.8	296	17.2	0.89	608
T-3	90 days	10.5	221	219	1210	72.3	ND	3100
	2 years	10.4	100	251	506	97.6	ND	1680

ND: not detected.

3.1.2. Evolution of the cement paste microstructure

The crystalline phases present in the cement pastes fabricated have been analysed by XRD analysis. Fig. 4 shows the XRD made in Ref sample and B-2 sample at 2, 7, 30 and 90 days. In the pastes based on OPC with mineral admixtures, the portlandite content decreases with curing time and has fully disappeared at 90 days in those with total silica content ≥55%, while in the reference sample the portlandite peaks even increase in size with hydration evolution. The peaks attributed to anhydrous grains of OPC, belite (C_2S) and alite (C_3S), are observed; although they are more clearly detected in the reference paste, they also exist in samples with a high content of mineral admixtures even at long ages. Peaks attributed to the ettringite could also be identified in all the pastes.

DTA/TG analyses confirm the results obtained by XRD and give some additional information. The endothermic peak of the portlandite (CH, between 400 and 500 °C) diminishes with the increase in the silica content of the binder and with age evolution in the low-pH cement pastes (B-1, B-2, T-2 and T-3); this peak completely disappearing at 90 days in those formulation with a silica content >55%. However, in the reference sample and in the paste with only 20% of mineral admixtures content (T-1) the portlandite content remains almost constant with time. These results do not agree with those published by Hong and Glasser [33] who determined that 15–20% cement replacement by SF should be enough to react with all portlandite but only if this mineral admixture is properly dispersed. However, in the evaluated pastes SEM observations have shown that the dispersion of the SF grains was not quite properly, as it is commented below.

Fig. 5 graphs the portlandite content for the six cement pastes at 90 days of curing, obtained using TG analysis. Although B-2 and T-3 show little weight loss in the TG analyses between 400 and 500 °C, the DTA of both pastes does not show the typical portlandite endothermic effect. Therefore, the weight loss observed in B-2 and T-3 pastes in this

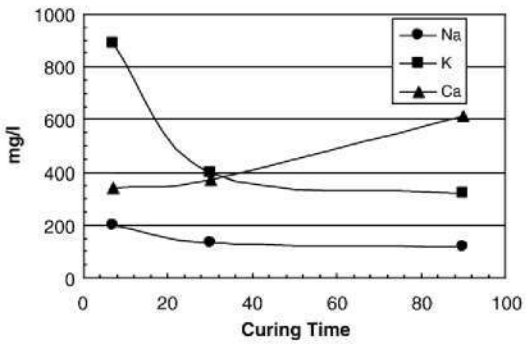

Fig. 3. Evolution of Na, K and Ca contents in the B-1 pore fluid.

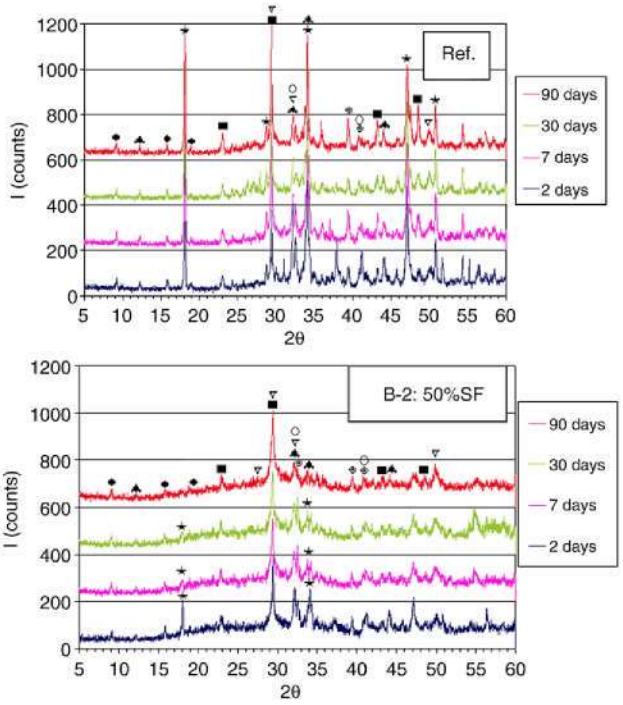

Fig. 4. XRD evolution of Ref (up) and B-2 (50%SF, down) pastes. CSH gel; $CaCO_3$; portlandite; C_2S; C_3S; C_4AF; quartz; ettringite.

temperature range can be attributed to dehydration of C–S–H gel and other hydrates, but not portlandite.

SEM data show cement pastes with a good texture and without an increase in micro-cracks comparing to the reference one. The amount of anhydrous cement grains is low and only composed of C_2S. SEM images also reveal the presence of non-reacted conglomerations of silica fume grains determining an incomplete dispersion of this mineral admixture which agrees with the higher percentage of SF needed to completely deplete the portlandite content, as it has been shown above. The C–S–H composition of cement pastes was studied using EDX microanalysis, resulting in CaO/SiO_2 ratios between 1.2 and 0.8 in the low-pH cement pastes (B-1, B-2, T-2 and T-3), whereas they were >1.5 in Ref and T-1 pastes. Although there is some residual portlandite in pastes B-1 and T-2 (detected by XRD and DTA/TG analyses), the measured C/S ratios are quite low. These results can be explained considering the heterogeneity of the sample (due to the incomplete SF dispersion previously commented) which would locally contain portlandite. Therefore in these two cement pastes possibly coexist zones near portlandite, whit higher C/S ratios, and zones near silica fume, where the pozzolanic reaction is more advanced, resulting in C–S–H with lower C/S ratios, being these last ones wider in the samples considering the pore fluid pH measured in both cement pastes (below 12.6).

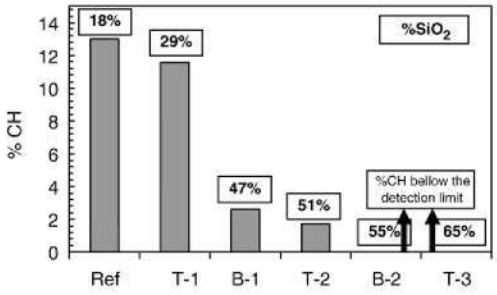

Fig. 5. Portlandite content of the cement pastes studied at 90 days (calculated from weigh loss obtained in TG analyses). Detection limit: 0.05%.

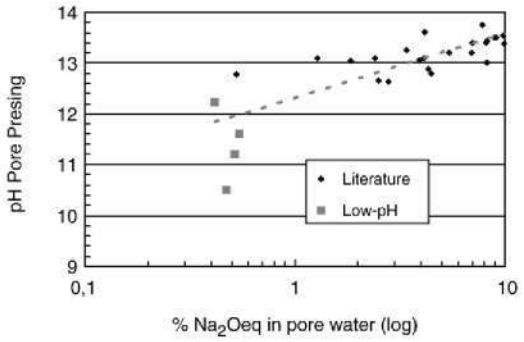

Fig. 6. Influence of Na_2Oeq on pH. Literature: [25,37–42].

3.1.3. Considerations when formulating low-pH binders

The introduction of high contents of mineral admixtures causes relevant changes in the microstructure of the cement pastes. The microstructure of the low-pH cement pastes is clearly different from the one typically found using standard OPC. For example, there is a great difference in the calcium silicate hydrates (C–S–H) generated, which is the main binding phase in all Portland cement-based systems. The C/S ratio of C–S–H in conventional Portland cement pastes varies from 1.2 to 2.3 [34], with a mean of 1.8 in Ref paste of the present work. On the contrary, in the low-pH cements this ratio (measured using SEM analyses) varies from 1.2 to 0.8. C–S–H gels with these CaO/SiO_2 ratios are typically considered to be formed by longer length chains of tetrahedral silica [35]. The C/S ratios found in the present work are in agreement with the work of Stronach and Glasser [36]. These authors indicated that to obtain a low pH in the cement materials the C/S ratio must be lower than 1.1.

Other important issue of the low-pH mixes is the decrease or disappearance of the CH content when using mineral admixtures with high silica content; in fact, in this work it has been demonstrated that increasing up to 45% the silica content in the binder formulation, the pore fluid pH can be reduced more than one unit. Furthermore, in reference OPC pastes the increase in the content of alkalis, Na and K, contributes to increase the pH in the pore water. However, if high contents of mineral admixtures are used, this general rule cannot be applied, as it can be seen in Fig. 6, as at lower alkali concentrations also the sulfate concentrations influence the pH values strongly.

But there is another important aspect regarding the alkali content in the pore fluid of low-pH OPC pastes. Taking into account that the alkali contents of mineral admixtures are similar (or higher in the case of the FA) than the OPC ones (see Table 1), it has to be emphasized that after 90 days and 2 years of hydration, there are less alkalis in the pore fluid of the low-pH cement pastes (see Table 5). This could be explained by considering that a binding process during hydration removes the alkalis from the pore solution of low-pH pastes. This binding would be taking place inside the new C–S–H gels. These results are in agreement with those published by Glasser and Marr in 1985 [43]; they said that SF is very effective in removing K from the pore fluid, due to the formation of smaller C/S ratios in the cement pastes. C–S–H gels with high C/S ratios have a positively charged surface, but as the C/S ratio decreases the charge becomes neutral, leaving Van Der Waals forces to operate, and at the lowest C/S ratios the surface charges of the pores become negative. In fact, Hong and Glasser [44] demonstrated that the alkali binding process is more effective when the C/S ratios of C–S–H gels are between 1.2 and 0.85, as it occurs in the low-pH cements of the present work. In the present work, the alkali content (both Na and K) in the aqueous phase of low-pH cement pastes is lower at longer times of curing, so it is possible that in the C–S–H gels the ions Na and K are gradually bonded and probably substituted by Ca in the pore solution, due to a need for electro-neutralization of the system, which agrees with the increase of Ca in the pore fluid (comparing low-pH cement pastes results with the reference ones) indicated in Table 4 at 90 days.

However, as all the low-pH cement pastes studied in the present work have SF in their composition, it should be considered that this alkali binding process can also take place on the surface of the non-reacted silica fume grains due to their known adsorption capacity [33,45–47].

3.2. Leaching of low-pH concretes with ground water form real repository conditions

3.2.1. Characterization of the leaching solution evolution

In a granitic HLRW repository the hydraulic conductivity of the low-pH concretes used has to be similar to that of the surrounding rock (which is in the order of 10^{-10} m/s). In the studied low-pH concretes, this parameter fulfils this requirement and it is stable along the test period, which indicates also a significant material stability. Observing Fig. 7 (left), it is remarkable that the hydraulic conductivity of the SC is slightly higher than the one of basic concrete, due to the increase in porosity generated in the material when shotcreting.

The pH values measured in the leachates obtained in the leaching test were never above 9 in all the cases and they are also very stable along the test period, as it can be seen in Fig. 7 (right). These values confirm that the low-pH shotcrete designed does not produce the alkaline plume generated by the interaction of the ground waters with the conventional concretes (based on OPC without mineral admixtures). Observing the modifications generated in the chemical composition of the leachates, (see Fig. 8 that shows the Ca and Mg contents but subtracting in each case the ion content of the ground water used), it is observed that the calcium content decreases at the beginning of the leaching test but increases with time after 100 days, whereas the magnesium one shows exactly the opposite behaviour. Their results, obtained using real groundwater as leaching agent, coincide with the decalcification processes reported in low-pH cementitious materials using pure water [9,13] or simulated fresh groundwater [9].

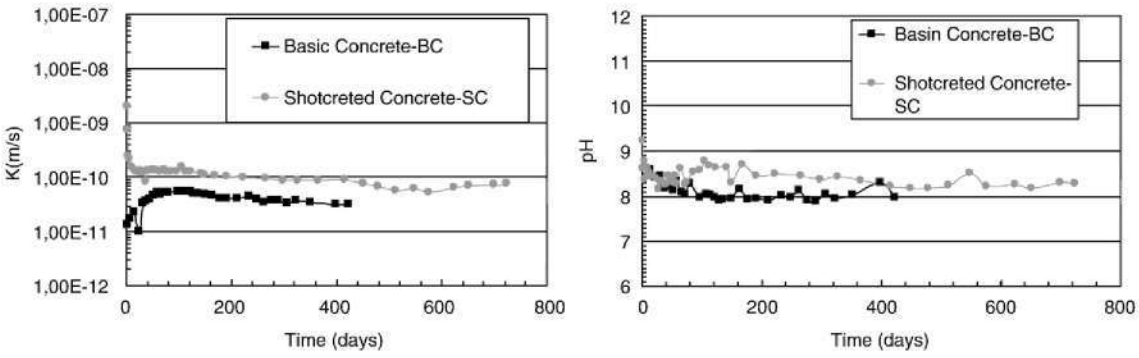

Fig. 7. Evolution with time of the hydraulic conductivity (left) and leachate pH (right) of the tested low-pH concretes.

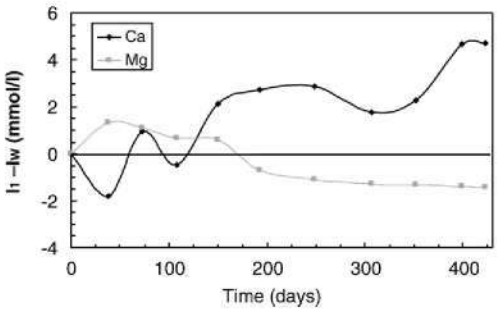

Fig. 8. Evolution with time of the Ca and Mg leachate contents (BC). I_l = ion content in leachate; I_w = ion content in the ground water used.

3.2.2. Evaluation of the degradation generated in the solid phases

Before the test, the concrete samples (both the BC and the SC ones) were characterised using BSEM. Concretes with a dense and homogeneous paste texture, good aggregate–paste interfaces and with presence of anhydrous phases (both anhydrous cement phases and non-reacted grains of SF) were observed. The CaO/SiO_2 ratio obtained in the C–S–H gels ranges between 0.65 and 0.7; it must be said that the silica content of these ratios was overestimated due to the size of the microanalysis area and the presence of small microsilica particles around all crystalline phases in the samples, but they are useful for comparison with those obtained in the tested samples.

After the leaching test period, first of all a phenolphtaleine test was carried out in the samples and a degradation front near the surface of the upper part could be visually observed using an optical microscope (identified as a decrease of pH<9 and no reaction with phenolphtaleine), as can be seen in Fig. 9, which shows the degradation front (bright zone) and the non-degraded concrete part (dark zone) of a BC sample after 14 months test. The thickness of the degradation front was higher in the SC samples (ranged between 650–750 μm in the BC samples and 1200–1500 μm in the SC samples) as the SC samples were exposed to ground water aggression during a longer period.

This degradation front can be also observed using BSEM. Fig. 10 shows a picture of the upper part of a SC sample after a 2-year period and the degraded zone (dark zone) near the surface is evident. In fact, combining BSEM observations with EDX analyses 2 zones with different characteristics can be defined in all the samples tested:

- *Degraded zone*: near the surface with a mean thickness of 700 μm ± 130 μm in the BC samples, and 1600 μm ± 270 μm in the SC samples. In this zone a decrease in the density of the paste and a calcite precipitation on the surface is observed. Furthermore, there are less anhydrous cement grains than before leaching test, the aggregates–paste interfaces are still good and there is not a significant increase in the number of micro-cracks. But the most relevant issue is the decalcification of the C–S–H gels in this degraded zone, obtaining C/S ratios between 0.25 and 0.6. Moreover, this decalcification is followed by an inclusion of Mg and also Cl^- in the solid phases, mainly in the C–S–H gels (both elements are supposed to come from the ground water used in the test; see the water composition in Table 4), but also the existence of magnesia nodules near the surface was observed. These results also agree with those reported by Fernandez et al. [48]: they demonstrated the inclusion of Mg into the C–S–H structure when magnesium oxide exists in the surrounding media, considering for cement pastes with low CaO/SiO_2<1 (as those of the present paper) the incorporation of these ions substituting calcium ions in the octahedral sites of the C–S–H gels or even forming a new phase attributed to the formation of a magnesium silicate hydrate (M–S–H). In the low-pH concretes evaluated in present paper "magnesia nodules" are also observed in the paste of the concrete. Therefore, the behaviour observed in the leaching composition (see Fig. 8), where an increase on the Ca content but a decrease in the Mg content with time are observed, combined with the evaluation of the solid phases, indicates that the decalcification generated by the leaching process can cause a "charge defect", that could be compensated by a progressive inclusion of Mg. Brew and Glasser also described that when cementitious materials react with Mg-containing ground waters (as in the present work), the presence of mineral admixtures with high silica content (as SF, FA or slags) enhances the appearance of M–A–H or M–S–H phases [49]. The M–S–H phases have been identified as an effective sorbent for potassium [50]. The presence of Cl^- from the groundwater in the solid phases has to be evaluated in depth.
- *Non-degraded zone*: that corresponds with the rest of the concrete samples or, in other words, the majority of the concrete sample. This part has a similar aspect and similar C/S ratios in the C–S–H gels than those observed in the same samples after testing, being only remarkable the decrease in the anhydrous cement grains presence.

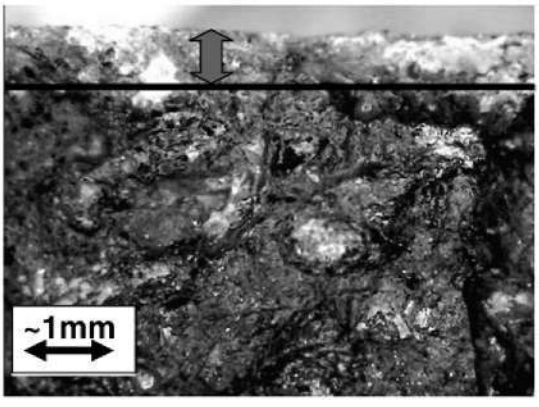

Fig. 9. Degradation front after 14 months. Optical microscopy observation. BC sample.

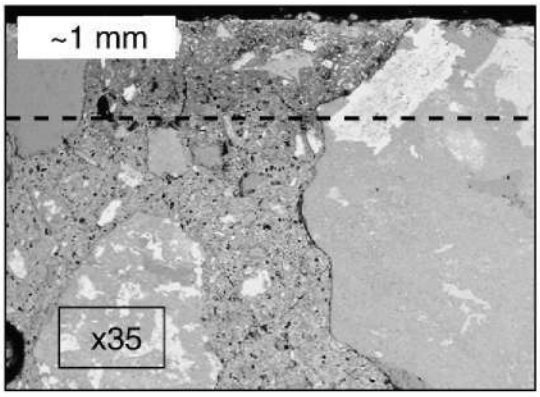

Fig. 10. Degradation front after 2 years. BSEM observation. SC sample.

Fig. 11 shows the EDX microanalyses profiles obtained in the pastes of the two types of concretes evaluated (BC and SC), presenting the modifications occurred with the depth of the samples in the C/S ratios of the C–S–H gels and in the magnesium and Cl^- concentrations. It is quite evident that near the surface, there is a decalcification of the C–S–H gels and solid phases rich in Mg and Cl^- compounds that come from the ground water used, although the Mg-rich zone is smaller than the decalcification one, and it seems to be limited to the surface of the sample. However, after this small zone, the rest of the paste of both types of concretes has a similar composition than those obtained before testing. Although the commented phenomena occurred in both types of concretes they are more evident in the cores extracted from the shotcreted plug (SC samples), as it can be seen in Fig. 11, as they were tested for longer time (2 years, whereas

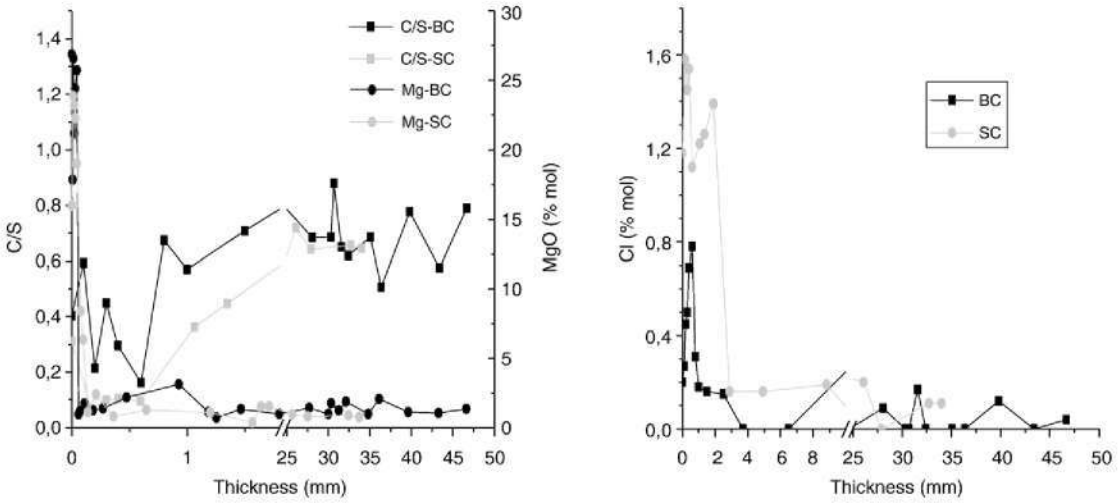

Fig. 11. EDX microanalyses profiles in concrete samples after leaching test. C/S: CaO/SiO_2 ratio of the cement paste; Mg: magnesium content of the cement paste.

the basic concrete samples, BC, were tested for 14 months). These C/S profiles agree with leaching tests results reported using a similar low-pH cement formulation but in this case the C/S ratios of the non-degraded zone are lower (it must be taking into account that leaching test from [13] were made in cement pastes and in present paper concrete specimens have been used).

4. Conclusions

From the results of this work it can be concluded that:

- The development of low-pH cement formulations based on OPC implies the use of mineral admixtures with high reactive silica content. The use of cement binders with high contents of mineral admixtures, mainly SF, produces low-pH pore waters. pH < 12 are measured in the present work.
- The microstructure of the low-pH cement pastes elaborated is different from that corresponding to conventional OPC pastes. The C–S–H generated with low-pH binders contains CaO/SiO_2 ratios between 1.2 and 0.8, or even lower in low-pH concrete samples.
- The alkali content in the pore water of low-pH cements is not a pH controlling factor as in conventional OPC materials, and it is possible that, in the C–S–H gels of the low-pH cements, the ions Na and K are gradually bonded and probably substitute Ca.
- Results of leaching tests show a good resistance of the produced low-pH concretes against ground water aggression, although an altered front can be observed from the surface in all the tested samples. In this altered front, the incorporation of magnesium ions from ground water into the C–S–H gels (possibly forming M–S–H phases) is suggested.

Acknowledgements

The authors are grateful to EU Project ESDRED (FI6W-CT-2004-508851) and ENRESA for their support of this work.

References

[1] S. Ramírez, J. Cuevas, R. Vigil, S. Leguey, Hydrothermal alteration of "La Serrata" bentonita (Almeria, Spain) by alkaline solutions, Appl. Clay Sci. 2 (2002) 257–269.
[2] A. Hidalgo, J.L. García, M.C. Cruz, L. Fernández, C. Andrade, Testing methodology for pH determination of cementitious materials. Application to low pH binders for use in HLNWR, R&D on Low-pH Cement for a Geological Repository. Workshop June (2005) Madrid, 2005.
[3] U. Vuorinen, J. Lehikoinen, Low-pH grouting cements—results of leaching experiments and modelling, R&D on Low-pH Cement for a Geological Repository. Workshop June (2005) Madrid, 2005.
[4] T. Hugo-Persson, B. Lagerblad, C. Vogt, Selective stabilization of deep core drilled boreholes using low-pH cement, R&D on Low-pH Cement for a Geological Repository. Workshop June (2005) Madrid, 2005.
[5] C. Cau Dit Coumes, S. Courtois, D. Nectoux, S. Leclerq, X. Bourbon, Formulating a low-alkalinity, high-resistance and low-heat concrete for radioactive waste repositories, Cem. Concr. Res. 36 (2006) 2152–2163.
[6] M. Nakayama, K. Iriya, A. Fujishima, M. Mihara, K. Hatanaka, Y. Kurihara, M. Yui, Development of low alkaline cement considering pozzolanic reaction for support system in HLW repository construction, Mater. Res. Soc. Symp. Proc. 932 (2006) 159–166.
[7] L.R. Dole, C.H. Mattus, Low pH concrete for use in the US high-level waste repository: Part I overview, Proc. R&D on Low-pH Cement for a Geological Repository, 3rd Workshop, June 13–14 Paris, 2007, pp. 31–39.
[8] J.L. García, M.C. Alonso, A. Hidalgo, L. Fernández Luco, Design of low-pH cementitious materials based on functional requirements, Proc. R&D on Low-pH Cement for a Geological Repository, 3rd Workshop, June 13–14 Paris, 2007, pp. 40–51.
[9] T. Yamamoto, H. Imoto, H. Ueda, M. Hironaga, Leaching alteration of cementitious materials and release of organic additives, Proc. R&D on Low-pH Cement for a Geological Repository, 3rd Workshop, June 13–14 Paris, 2007, pp. 52–62.
[10] C.H. Mattus, L.R. Dole, Low pH concrete for use in a US high-level waste repository: Part I:-Formulation and tests, Proc. R&D on Low-pH Cement for a Geological Repository, 3rd Workshop, June 13–14 Paris, 2007, pp. 72–82.
[11] M. Vuorio, J. Hansen, Long-term safety and durability related studies on low-pH grouting materials, Proc. R&D on Low-pH Cement for a Geological Repository, 3rd Workshop, June 13–14 Paris, 2007, pp. 83–88.
[12] Y. Kobayashi, T. Yamada, H. Matsui, M. Nakayama, M. Mihara, M. Naito, M. Yui, Development of low-alkali cement for application in a JAEA URL, Proc. R&D on Low-pH Cement for a Geological Repository, 3rd Workshop, June 13–14 Paris, 2007, pp. 98–106.
[13] M. Codina, C. Cau-dit-Coumes, P. Le Bescop, J. Verdier, J.P. Ollivier, Design and characterization of low-heat and low-alkalinity cements, Cem. Concr. Res. 38 (4) (2008) 437–448.
[14] M.N. Gray, B.S. Shenton, For better concrete, take out some of the cement, Proc. 6th ACI/CANMET Symposium on the Durability of Concrete, Bangkok, Thailand, May 31 to June 5, 1998, 1998.
[15] K. Iriya, A. Matsui, M. Mihara, Study on applicability of HFSC for radioactive waste repositories, Radioactive Waste Management and Environmental Remediation, ASME Conference, Nagoya, Japan, September 16–30, 1999, 1999.
[16] M.C. Braney, A. Haworth, N.L. Jefferies, A.C. Smith, A study of the effects of an alkaline plume from a cementitious repository on geological materials, J. Contam. Hydrol. 13 (1993) 379–402.
[17] F. Adenot, M. Buil, Modelling of the corrosion of the cement paste by deionized water, Cem. Concr. Res. 22 (1992) 489–496.
[18] F.P. Glasser, M. Atkins, Cements in radioactive waste disposal, Mater. Res. Soc. Bull. 12 (1994) 33–39.
[19] P. Lovera, F. Adenot, M. Jorda, R. Cabrillac, Physico-chemical transformation of sulfated compounds during the leaching of highly sulfated cemented wastes, Cem. Concr. Res. 57 (27) (1997) 1523–1532.
[20] P. Faucon, F. Adenot, J.F. Jacquinot, J.C. Petit, R. Cabrillac, M. Jorda, Long-term behaviour of cement pastes used for nuclear waste disposal: review of physico-chemical mechanisms of water degradation, Cem. Concr. Res. 28 (1998) 847–857.
[21] T. Saeki, P.J.M. Monteiro, A model to predict the amount of calcium hydroxide in concrete containing mineral admixtures, Cem. Concr. Res. 35 (2005) 1914–1921.
[22] T.G. Durning, M.C. Hicks, Using microsilica to increase concrete's resistance to aggressive chemicals, Concr. Int. 13 (1991) 42–48.
[23] K. Torii, M. Kawamura, Effects of fly ash and silica fume on the resistance of mortar to sulfuric acid and sulfate attack, Cem. Concr. Res. 24 (1994) 361–370.
[24] C. Cau Dit Coumes, M. Sorgenti, S. Prené, X. Bourbon, Formulating a low-alkalinity and low-heat cement: Literature Review, R/D program and preliminary results,

Proc. Qualification of Low-pH Cement for a Geological Repository Workshop, Stockholm, Suède, October 15–16, 2003.
[25] P. Longuet, L. Burglen, A. Zelwer, The liquid phase of hydrated cement, Rev. Matér. Constr. Trav. Publics 676 (1973) 35–41.
[26] R.S. Barneyback, S. Diamond, Expression and analysis of pore fluids from hardened cement pastes and mortars, Cem. Concr. Res. 11 (1981) 279–285.
[27] J.L. García Calvo, M.C. Alonso, L. Fernández Luco, A. Hidalgo, M. Sánchez, Implications of the use of low-pH cementitious materials in HARW repositories, in: G. Bäckblom (Ed.), Proceedings of International Event, Conrox AB, Prague, 2008, pp. 213–224.
[28] J.A. Larbi, A.L.A. Fraay, J.M.M. Bijeri, The chemistry of the pore fluid of silica fume-blended cement systems, Cem. Concr. Res. 20 (1990) 506–516.
[29] M. Mihara, K. Iriya, A. Neyama, M. Ito, Experimental and modelling studies on the interaction between cement paste with silica fume and distilled water, Radioactive Waste Research, Atomic Energy Society of Japan, Tokyo, Japan, vol. 2, 1997, pp. 71–79.
[30] M.H. Shehata, M.D.A. Thomas, R.F. Bleszinski, The effects of fly ash composition on the chemistry of pore solution in hydrated cement pastes, Cem. Concr. Res. 29 (1999) 1915–1920.
[31] K. Torii, K. Taniguchi, M. Kawamura, Sulfate resistance of high fly ash content concrete, Cem. Concr. Res. 25 (4) (1995) 759–768.
[32] V.G. Papadakis, Effect of fly ash on Portland cement systems – Part I – low calcium fly ash, Cem. Concr. Res. 19 (1999) 1915–1920.
[33] S.-Y. Hong, F.P. Glasser, Alkali sorption by C–S–H gels. Part II. Role of alumina, Cem. Concr. Res. 32 (2002) 1101–1111.
[34] I. Klur, B. Pollet, J. Virlet, A. Nonat, in: P. Colombet (Ed.), C–S–H structure evolution with calcium content by multinuclear NMR, Springer, Berlin, 1998, pp. 119–141.
[35] X. Cong, R.J. Kirkpatrick, 29Si MAS NMR study of the structure of calcium silicate hydrate, Adv. Cem. Based Mater. 3 (3/4) (1996) 144–156.
[36] S.A. Stronach, F.P. Glasser, Modelling the impact of abundant geochemical components on phase stability and solubility of the $CaO–SiO_2–H_2O$ system at 25 °C: Na^+, K^+, SO_4^{2-}, Cl^- and CO_3^{2-}, Adv. Cem. Res. 9 (1997) 167S–181S.
[37] Diamond, Effects of two Danish flyashes on alkali contents of pore solutions of cement-flyash pastes, Cem. Concr. Res. 11 (1981) 383–394.
[38] F.P. Glasser, J. Marr, The effect of mineral additives on the composition of cement pore fluids, Proc. Br. Ceram. Soc. 35 (1984) 404–429.
[39] K. Andersson, B. Allard, M. Bengtsson, B. Magnusson, Chemical composition of cement pore solutions, Cem. Concr. Res. 19 (1989) 327–332.
[40] Nearfield behaviour of clay barriers and their interaction with concrete. Task 3 Characterisation of radioactive waste forms., A series of final reports (1985–89). Contract N° FI1W-00031. Final report. EUR 13877EN, 1991.
[41] P. Lorenzo, S. Goñi, S. Hernandez, A. Guerrero, Effect of fly ashes with high total alkali content on the alkalinity of the pore solution of hydrated Portland cement paste, J. Am. Ceram. Soc. 79 (1996) 470–474.
[42] A. Hidalgo, M. Castellote, I. Llorente, C. Alonso, C. Andrade, Effects of cement on clay barrier performance. ECOCLAY project., Final report. Contract N°. FI4W-CT96-0032. EURATOM. EUR 19609EN, 2002.
[43] F.P. Glasser, J. Marr, The alkali binding potential of OPC and blended cements, Il Cemento 82 (1985) 85–94.
[44] S.Y. Hong, F.P. Glasser, Alkali binding in cement pastes Part I. The C–S–H phase, Cem. Concr. Res. 29 (1999) 1893–1903.
[45] M.C.G. Juenger, C.P. Ostertag, Alkali-silica reactivity of large silica fume derived particles, Cem. Concr. Res. 34 (2004) 1389–1402.
[46] J.A. Larbi, A.L.A. Fraay, J.M.J.M. Bijen, The chemistry of the pore fluid of silica fume-blended cement systems, Cem. Concr. Res. 20 (1990) 506–516.
[47] D. Bonen, S. Diamond, Occurrence of large silica fume-derived particles in hydrated cement paste, Cem. Concr. Res. 22 (1992) 1059–1066.
[48] L. Fernández, C. Alonso, C. Andrade, A. Hidalgo, The interaction of magnesium in hydration of C3S and C–S–H formation using 29Si MAS-NMR, J. Mater. Sci. 43 (2008) 5772–5783.
[49] D.R.M. Brew, F.P. Glasser, Synthesis and characterization of magnesium silicate hydrate gels, Cem. Concr. Res. 35 (2005) 85–98.
[50] D.R.M. Brew, F.P. Glasser, The magnesia-silica gel phase in slag cements: alkali (K, Cs) sorption potential of synthetic gels, Cem. Concr. Res. 35 (2005) 77–83.